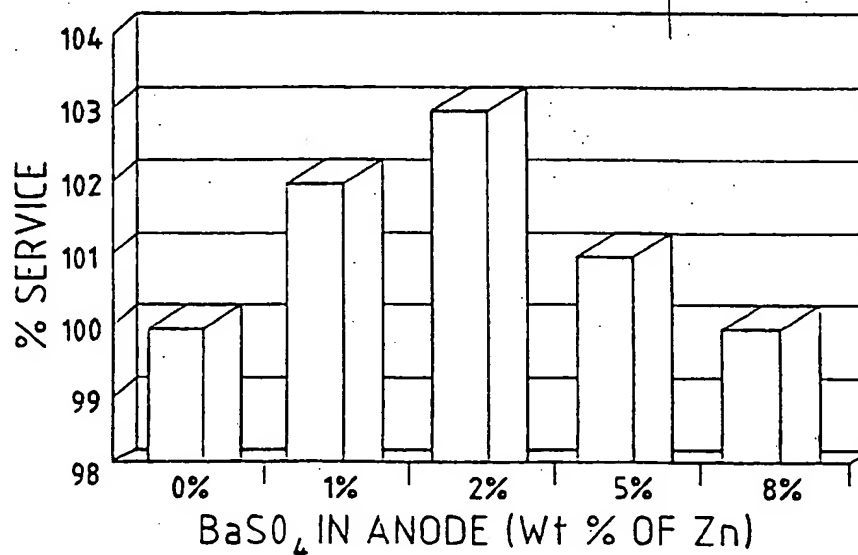


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(54) Title: ELECTROCHEMICAL CELL HAVING ELECTRODE ADDITIVES



(57) Abstract

An electrochemical cell is provided having an anode, a cathode and an electrolyte, the anode and optionally the cathode comprising a barium compound such as barium sulphate (BaSO₄) or barium hydroxide (Ba(OH)₂) as an additive. Alternatively, the cathode comprises barium hydroxide (Ba(OH)₂) as an additive. The anode comprises an anode active material such as zinc, and the cathode comprises a cathode active material such as manganese dioxide, preferably electrolytic manganese dioxide. Also provided is a method of treating active material by mixing with the barium compound additive and drying the mixture. The anode and cathode are particularly adapted for use in an electrochemical cell having an alkaline electrolyte. The barium compound additive provides improved service performance for the cell.

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ELECTROCHEMICAL CELL HAVING ELECTRODE ADDITIVES

5 This invention generally relates to electrochemical cells including electrode additives, such as alkaline electrochemical cells having cathodes formed of manganese dioxide and anodes formed of zinc. In particular, the invention relates to electrochemical cells having electrode active material that includes barium compounds as additives.

10

 Conventional alkaline cells generally include a steel cylindrical can having a cathode comprising manganese dioxide as the active material and formed on the interior surface of the steel can, an anode comprising zinc powder and located in the centre of the cell, a separator located between the anode and the cathode, and an alkaline
15 electrolyte solution simultaneously contacting the anode, the cathode, and separator. A conductive current collector is commonly inserted into the anode active material and a seal assembly provides closure to the open end of the steel can.

 A primary goal in designing alkaline battery cells is to increase the service
20 performance of the cell. The service performance is the length of time for the cell to discharge under a given load to a specific voltage at which the cell is no longer useful for its intended purpose. One approach taken to increase service performance has been to increase the interior volume of the cell in order to increase the amount of active materials within the cell. However, the commercial external size of the cell is generally
25 fixed, thereby limiting the ability to increase the amount of active materials within the cell.

 Another approach taken to increase the service performance of a cell is to utilise additives within the electrodes of the cell. For example, US-A-5,599,644 discloses the
30 use of tin dioxide (SnO_2), and other similar materials in the cathode. Another example is disclosed in WO-A-93/12551. This reference teaches the use of a barium compound

additive such as barium sulphate (BaSO_4) in an amount of 3% to 25% in the cathode of an electrochemical cell. The additives discussed in both references provide for enhanced service performance. Despite past increases in the service performance, the need to find new ways to increase service performance remains the primary goal of cell designers.

5

We have now found, surprisingly, that the service performance of an alkaline electrochemical cell may be improved by the addition of a barium compound to the anode only, or to both the anode and the cathode. Alternatively, a specific barium compound may be added to the cathode only. We have also found that the barium compound is preferably added by impregnating the electrode active material with the barium compound, for example by impregnating an anode active material such as zinc, or a cathode active material such as manganese dioxide, or both, with the barium compound.

10

15

Accordingly, in a first aspect, the present invention provides an electrochemical cell having an anode, a cathode and an electrolyte, the anode comprising anode active material and a barium compound as an additive. According to this aspect, the additive is added to the anode active material before or during assembly of the cell. The additive is preferably barium sulphate (BaSO_4), more preferably barium hydroxide ($\text{Ba}(\text{OH})_2$).

20

In one embodiment of the first aspect, a barium compound is added only to the anode as an additive. In an alternative embodiment, the cathode also comprises a barium compound added to the cathode as an additive.

25

In a second aspect, the present invention provides an electrochemical cell having an anode, a cathode and an electrolyte, the cathode comprising cathode active material and barium hydroxide ($\text{Ba}(\text{OH})_2$) as an additive.

30

In a third aspect, the present invention provides a method of preparing an electrochemical cell having an anode, a cathode and an electrolyte, the anode comprising anode active material and a barium compound as an additive, comprising the steps of mixing the anode active material and the barium compound to form a mixture, and

drying the mixture. According to this aspect, the mixture is prepared before being incorporated into the cell.

Furthermore, in a fourth aspect, the present invention provides a method of
5 preparing an electrochemical cell having an anode, a cathode and an electrolyte, the
cathode comprising cathode active material and a barium compound as an additive,
comprising the steps of mixing the cathode active material and the barium compound to
form a first mixture, and drying the first mixture. Preferably the dried first mixture is
then mixed with a solution of a strong acid, preferably sulphuric acid, to form a second
10 mixture, followed by drying of the second mixture. According to this aspect, at least the
first mixture is prepared before being incorporated into the cell.

The present invention advantageously provides for enhanced service performance
by employing an anode containing a barium compound, preferably barium sulphate,
15 more preferably barium hydroxide, as an additive, in accordance with the first aspect.
Where the anode active material comprises zinc and the barium compound is barium
sulphate or barium hydroxide, preferably the barium sulphate or barium hydroxide
additive is present in the anode in the amount of up to 8% by weight of zinc.

20 The present invention further advantageously provides for increased service
performance by employing a barium compound, preferably barium sulphate, more
preferably barium hydroxide, as an additive in both the anode and cathode of the cell,
according to another embodiment of the first aspect. According to this embodiment,
superior performance results may be achieved by employing the additive in an amount
25 of approximately 2% by weight of active electrode materials in each of the anode and
cathode.

Superior performance results may also be achieved by employing a cathode
containing barium hydroxide as an additive, according to the second aspect of the
30 present invention.

The anode comprises an anode active material such as zinc, and is preferably formed of zinc powder, a gelling agent, and additives.

5 The cathode comprises a cathode active material such as manganese dioxide (MnO_2), and preferably comprises electrolytic manganese dioxide (EMD) as the electrochemically active material. The cathode is preferably formed of a mixture of manganese dioxide, graphite, 45% potassium hydroxide solution, deionised water, and aqueous Teflon® solution comprising approximately 20% polytetrafluoroethylene, and additives.

10

The anode and cathode of the present invention are particularly adapted for use in an electrochemical cell having an alkaline electrolyte. The electrolyte is preferably alkaline, and more preferably is formed of potassium hydroxide (KOH).

15

Preferably, the cell is a cylindrical cell, more preferably a cylindrical cell that includes a steel can, although it should be appreciated that other cell configurations may be used.

20

It should be appreciated that the electrochemical cell of the present invention has a barium compound such as barium sulphate or barium hydroxide employed in the anode according to one embodiment of the first aspect, contains a barium compound such as barium sulphate or barium hydroxide employed in both the anode and the cathode according to another embodiment of the first aspect, and contains barium hydroxide employed in the cathode according to the second aspect.

25

In one embodiment of the first aspect, an electrochemical cell is provided having an anode comprising a zinc active material and, as an anode additive, barium sulphate or, more preferably, barium hydroxide, in an amount up to 8% by weight of zinc active material.

30

According to another embodiment of the first aspect, the cathode of the electrochemical cell comprises an active cathode material such as manganese dioxide,

and also has a barium compound such as barium sulphate or barium hydroxide as an additive. Thus, in a preferred embodiment, an electrochemical cell is provided having an anode comprising a zinc active material and, as an anode additive, a barium compound, and further having a cathode comprising a manganese dioxide active material and, as a cathode additive, a barium compound.

In a preferred embodiment of the first aspect, the anode additive comprises approximately 2% by weight of the anode active material, and the cathode additive comprises approximately 2% by weight of the cathode active material. Preferably, the barium additive is barium sulphate, more preferably barium hydroxide. Therefore, in a more particular preferred embodiment, an electrochemical cell is provided having an anode, a cathode and an electrolyte, the cathode comprising a manganese dioxide active material and a cathode additive, the cathode additive comprising approximately 2% barium sulphate or barium hydroxide by weight of the cathode active material, the anode comprising a zinc active material, and an anode additive, the anode additive comprising approximately 2% barium sulphate or barium hydroxide by weight of the anode active material.

In an embodiment of the present invention related to the third aspect, a method of treating an active material of an anode of an electrochemical cell is provided comprising the steps of mixing an anode active material, preferably comprising zinc, and a barium additive and drying the mixture. Preferably, the method further comprises the step of blending the dried mixture into a dry anode mix or, alternatively, into a gelled electrolyte. The barium additive comprises preferably barium sulphate, more preferably barium hydroxide.

In an embodiment of the present invention related to the fourth aspect, a method of treating an active material of a cathode of an electrochemical cell is provided comprising the steps of mixing a cathode active material and a barium additive to form a first mixture and drying the first mixture. Preferably, the method further comprises the steps of mixing the first mixture with a solution of a strong acid, preferably comprising sulphuric acid (H_2SO_4), forming a second mixture and drying the second mixture. The

barium additive comprises preferably barium sulphate, more preferably barium hydroxide. The cathode active material preferably comprises electrolytic manganese dioxide (EMD).

5 In further embodiments, the anode comprises zinc and the cathode comprises electrolytic manganese dioxide (EMD), and the present invention employs methods for treating the zinc of the anode and impregnating the EMD of the cathode with the barium additive, preferably barium sulphate or barium hydroxide, and most preferably barium hydroxide.

10

The present invention will be further understood by reference to the appended drawings, in which:

Figure 1 is a cutaway perspective view of an example of an electrochemical cell constructed in accordance with the present invention;

15

Figure 2 is a bar graph comparing the percent service performance measured for alkaline electrochemical cells having an anode with different amounts of barium sulphate additive;

Figure 3 is a graph further illustrating measured service performance of the alkaline electrochemical cells having an anode with a barium sulphate additive;

20

Figure 4 is a bar graph comparing the percent service performance of electrochemical cells having a cathode with different amounts of barium sulphate additive;

Figure 5 is a graph further illustrating measured service performance of the alkaline electrochemical cells having a cathode with different amounts of barium sulphate additive;

25

Figure 6 is a comparative graph illustrating service performance of a standard alkaline cell having no additives as compared to an electrochemical cell having an anode with barium sulphate additive, and an electrochemical cell having both the anode and cathode containing barium sulphate additive;

30

Figure 7 is a flowchart illustrating a method of treating zinc for use in the anode with a barium compound, specifically barium hydroxide, to increase anode performance; and

Figure 8 is a flowchart illustrating a method of impregnating a barium compound, specifically barium hydroxide, into the pores of electrolytic manganese dioxide (EMD) to increase performance of the cathode.

- 5 Referring to Figure 1, a cutaway view of a cylindrical alkaline electrochemical cell 10 is shown therein. Alkaline cell 10 includes a steel can 12 having a cylindrical shape with a closed bottom end and an open top end. A metalised, plastic film label 14 is formed about the exterior surface of steel can 12, except for the ends of steel can 12. At the closed end of steel can 12 is a positive cover preferably formed of plated steel.
- 10 Film label 14 is formed over the peripheral edge of positive cover 16.

- A cathode 20, preferably formed of a mixture of manganese dioxide, graphite, 45% potassium hydroxide solution, deionised water, and aqueous Teflon® solution comprising approximately 20% polytetrafluoroethylene, and additives, is formed about
- 15 the interior surface of steel can 12. Separator 22, which is preferably formed of a non-woven fabric that prevents migration of any solid particles in the cell, is disposed about the interior surface of cathode 20. An electrolyte 24 formed of potassium hydroxide (KOH) is disposed in the can 12, preferably within the interior of separator 22. An
- 20 anode 18, preferably formed of zinc powder, a gelling agent, and additives is disposed within electrolyte 24 in contact with a current collector 26, which may include a brass nail. Accordingly, the cathode 20 is configured as the cell's positive electrode, and the anode 18 is configured as the cell's negative electrode.

- Current collector 26 contacts a brass rivet 28 formed at the open end of steel can
- 25 12. A nylon seal 30 is formed at the open end of steel can 12 to prevent leakage of the active ingredients contained in steel can 12. Nylon seal 30 contacts a metal washer 28 and an inner cell cover 34, which is preferably formed of steel. A negative cover 36, which is preferably formed of plated steel, is disposed in contact with current collector 26 via a weld. Negative cover 36 is electrically insulated from steel can 12 by nylon
- 30 seal 30.

The anode 18 preferably contains zinc powder as the electrochemically active material. In addition, in one embodiment according to the first aspect, the anode 18 contains an anode additive material that has a barium compound, and more preferably includes a barium sulphate (BaSO_4) or, most preferably, a barium hydroxide ($\text{Ba}(\text{OH})_2$) additive. The cathode 20 preferably contains manganese dioxide (MnO_2), more preferably electrolytic manganese dioxide (EMD), as the electrochemically active material. In addition, in another embodiment according to the first aspect, the cathode 20 also contains a barium compound, and more particularly has a barium sulphate (BaSO_4) or, most preferably, a barium hydroxide ($\text{Ba}(\text{OH})_2$), as a cathode additive. Alternatively, in an embodiment according to the second aspect, the cathode 20 contains barium hydroxide ($\text{Ba}(\text{OH})_2$) as a cathode additive.

According to a preferred embodiment of the first aspect of the present invention, the anode of the electrochemical cell contains barium sulphate or barium hydroxide additive in the amount of 8% or less by weight of anode active materials. Accordingly, zinc cell 10 contains an amount of barium sulphate or barium hydroxide no greater than 8% by weight of the amount of zinc employed in the anode 18.

Examples of D-size zinc/manganese dioxide alkaline electrochemical cells were assembled containing different amounts of barium sulphate or barium hydroxide additive in the anode 18. The bar graph shown in Figure 2 illustrates examples of electrochemical cells and shows a conventional cell having no barium sulphate additive (0%) to those cells having barium sulphate additive to the anode 18 in the amounts of 1%, 2%, 5%, and 8% by weight of total zinc in the anode. In the comparative examples shown, the D-size cells were tested with an intermittent discharge of one hour per day at a resistance of 2.2 ohms, and the service performance cut-off was measured at 0.8 volts. In contrast to the control cell having no barium sulphate, it was discovered that the use of barium sulphate additive to the anode 18 in the amount of up to 8% by weight of the anode active material realised an increase in the service performance of the cell. The greatest performance increase is shown with approximately 2% barium sulphate additive by weight percent of zinc.

Referring to Figure 3, the effects of the barium sulphate additive to anode 18 for the examples provided in Figure 2 were measured and plotted for both amp hours as represented by line 40, and amp hours per gram of zinc as represented by line 42. Both the measured amp hours data 40 and amp hours per gram of zinc data 42 show an increase in the cell's current performance for amounts of barium sulphate additive up to 8% by weight of zinc in the anode 18.

Barium hydroxide was also used as the additive to anode 18. When D-size cylindrical cells with the treated barium hydroxide additive were tested, an 8% increase in cell performance compared to the D-size cylindrical cells without the barium hydroxide on a 500 mA continuous discharge test to a 1.0 V cut-off. At a 0.9 V cut-off, a 6% increase in performance was observed. At the 0.8 V and 0.75 V cut-offs, 3% and 2% respective increases in performance were observed.

Referring to Figure 4, the effect of adding barium sulphate additive to the cathode 20 was determined by evaluating different amounts of barium sulphate by weight percent of electrolytic manganese dioxide (EMD) in the cathode 20. The cells tested were D-size cylindrical cells, tested intermittently by discharging one hour per day at a resistance of 2.2 ohm to a voltage cut-off of 0.8 volts. As shown, the addition of barium sulphate additive to the cathode 20 provided a service performance increase when used in the amount of up to approximately 10.2% by weight of total EMD. It was realised that significant service performance increases could be realised in the amount of up to 2.9% barium sulphate additive by weight percent of the EMD in the cathode 20.

The effect of the barium sulphate additive on the D-size cells shown in Figure 4 is further illustrated in Figure 5. As shown, line 44 represents the measured amps hours and line 46 represents the measured amp hours per gram of EMD. The graph shows that an increase in amps hours and amp hours per gram is realised with barium sulphate additive in the amount of up to 10.2% by weight percent of EMD in the cathode 20.

According to another embodiment of the first aspect of the present invention, both the anode 18 and cathode 20 of electrochemical cell 10 contain barium sulphate or

barium hydroxide additive to achieve enhanced service performance of the cell 10. According to this embodiment, barium sulphate or barium hydroxide is added to the anode in the amount of approximately 2% by weight of active anode material (zinc), and barium sulphate is also added to the cathode in the amount of 2% by weight of active
5 cathode material (manganese dioxide).

A D-size cylindrical cell was assembled and tested by being intermittently discharged one hour per day at a resistance to 2.2 ohms, and the voltage measurement is shown in Figure 6. The service performance realised for the electrochemical cell
10 containing barium sulphate in both the anode and cathode is represented by line 52. In contrast, the service performance realised with a similar cell having barium sulphate in the anode only is shown by line 54. As a comparison, a control cell was constructed having no barium sulphate in either the anode or cathode, and its test results are shown by line 50. According to this experiment, the cell containing barium sulphate in both
15 the anode and cathode realised an increase in the average service performance of D-sized cells, according to this test, by as much as 13%, as compared to the average performance of the control cell having no barium sulphate additive.

Figure 7 shows the process 300 for impregnating/coating zinc used in an anode
20 of the present invention with barium additive, specifically barium hydroxide. In step 60, the type and amount of zinc to be treated is determined. Next, in step 62, a solution of 0.2M barium hydroxide and deionised water is made by mixing 63.1 grams of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ with 950 ml of deionised water to make a 1000 ml solution. In step 64, 1000 ml of the 0.2M barium hydroxide solution is added to 3150 grams of zinc 64. The
25 wetter mixture of barium hydroxide solution and zinc is mixed in step 66, allowed to air dry in step 68 for two hours, and dried in a 71°C oven for 18 hours in step 70. In decision block 72, it is determined whether at this point the solution is dry and, if not, then the mixing and drying steps represented by steps 66, 68 and 70 are repeated. If the solution is dry, then the barium coated zinc is either dry blended or blended into the
30 gelled electrolyte 74.

To dry blend large batches of anode mix, the barium coated zinc may be blended using a conventional multiple blade blender, while small anode mixes may be made by vigorously shaking the anode components in a polymeric container to achieve a homogenous mixture.

5

For example, to mix a large batch, first add the treated zinc, Carbopol® and indium hydroxide ($\text{In}(\text{OH})_3$) to a blender and dry blend for three to five minutes at medium speed. Stop the blending and scrape down the sides. Next, restart the blender and add 0.1N KOH with the blender running. Blend for an additional three to five
10 minutes. Again, stop blending and scrape down the sides. With the blender running, add a 40% KOH solution, which may also contain conventional additives. Blend for at least ten additional minutes stopping and scraping down the sides of the container as needed. Turn off the blender and place the anode material into the appropriate polypropylene container. Continue blending the anode mix for five minutes to achieve a
15 homogenous mixture. This last step reduces the amount of lumps in the anode mix.

To mix a smaller batch of anode mix, for example, add the treated zinc, Carbopol®, and indium hydroxide ($\text{In}(\text{OH})_3$) to a suitable polymeric container. Next, seal the container and shake for at least two minutes until the dry components are
20 uniformly mixed. Add the 0.1N KOH solution to the 40% KOH solution to form the total quantity of KOH solution. Next, add the total quantity of KOH solution, which may also contain conventional additives, and shake for one minute. Lastly, the solution is mixed for two minutes.

25 Figure 8 illustrates a method according to an embodiment of the fourth aspect of the present invention, and shows a process 200 for impregnating the electrolytic manganese dioxide (EMD) for use in a cathode with a barium additive, specifically barium hydroxide. First in step 80, the total amount of manganese dioxide needed is determined. Step 82 involves mixing the MnO_2 with a 0.2M barium hydroxide solution.
30 The barium hydroxide solution may be prepared in the same manner as it was prepared in step 62 in the zinc treating process 300. The mixture is allowed to air dry in step 84. After that, during step 86, the mixture is placed in a 71°C oven for a period of time

12

sufficient to dry the mixture. Decision block 88 involves determining whether there is a layer of barium hydroxide powder on the dried mixture. If there is a layer of barium hydroxide powder, then the barium hydroxide powder must be broken up and remixed with deionised water in step 91, and allowed to air dry in step 92. This process is repeated until there is no barium hydroxide powder on top of the hard crust of the manganese dioxide and barium hydroxide mixture indicating that a good mixture has been achieved. Once a good mixture is achieved, in step 94, the mixture is broken up into a loose powder. Optionally, a solution of 0.2M sulphuric acid is added to the dry mixture in step 96. Following step 96, the mixture is allowed to air dry in step 98.

10

From this point, as shown in step 100, the cathode mix is ready for use in electrochemical cells using normal techniques as are conventional and known to one of the ordinary skill in the art.

CLAIMS:

1. An electrochemical cell having an anode, a cathode and an electrolyte, the anode comprising anode active material and a barium compound as an additive.
5
2. An electrochemical cell according to claim 1, wherein the barium compound is selected from barium sulphate (BaSO_4), barium hydroxide (Ba(OH)_2), and mixtures thereof.
- 10 3. An electrochemical cell according to claim 2, wherein the barium compound in the anode is barium hydroxide (Ba(OH)_2).
4. An electrochemical cell according to any preceding claim, wherein the anode comprises the barium compound in an amount of up to 8% by weight of the anode active
15 material.
5. An electrochemical cell according to any preceding claim, wherein the anode active material comprises zinc.
- 20 6. An electrochemical cell according to any preceding claim, wherein the cathode comprises cathode active material and a barium compound as an additive.
7. An electrochemical cell according to claim 6, wherein the barium compound in the cathode is selected from barium sulphate (BaSO_4), barium hydroxide (Ba(OH)_2), and
25 mixtures thereof.
8. An electrochemical cell according to claim 7, wherein the barium compound in the cathode is barium hydroxide (Ba(OH)_2).
- 30 9. An electrochemical cell having an anode, a cathode and an electrolyte, the cathode comprising cathode active material and barium hydroxide (Ba(OH)_2) as an additive.

10. An electrochemical cell according to any of claims 6 to 9, wherein the cathode comprises the barium compound in an amount of up to 8% by weight of the cathode active material.

5

11. An electrochemical cell according to any of claims 6 to 8, wherein the cathode comprises the barium compound cathode additive in an amount of approximately 2% by weight of the cathode active material, and the anode comprises the barium compound anode additive in an amount of approximately 2% by weight of the anode active material.

10

12. An electrochemical cell according to any preceding claim, wherein the cathode active material comprises manganese dioxide, preferably electrolytic manganese dioxide (EMD).

15

13. A method of preparing an electrochemical cell having an anode, a cathode and an electrolyte, the anode comprising anode active material and a barium compound as an additive, comprising the steps of mixing the anode active material and the barium compound to form a mixture, and drying the mixture.

20

14. A method according to claim 13, wherein the anode active material comprises zinc.

15. A method according to claim 13 or claim 14, further comprising the step of blending the dried mixture into a dry anode mix.

25

16. A method according to claim 13 or claim 14, further comprising the step of blending the dried mixture into a gelled electrolyte.

17. A method of preparing an electrochemical cell having an anode, a cathode and an electrolyte, the cathode comprising cathode active material and a barium compound as

30

an additive, comprising the steps of mixing the cathode active material and the barium compound to form a first mixture, and drying the first mixture.

18. A method according to claim 17 further comprising the steps of mixing the first mixture with a solution of a strong acid to form a second mixture, and drying the second mixture.

19. A method according to claim 18, wherein the strong acid comprises sulphuric acid (H_2SO_4).

10

20. A method according to any of claims 17 to 19, wherein the cathode active material comprises electrolytic manganese dioxide.

21. A method according to any of claims 17 to 20, wherein the barium compound is barium sulphate (BaSO_4).

15

22. A method according to any of claims 17 to 20, wherein the barium compound is barium hydroxide ($\text{Ba}(\text{OH})_2$).

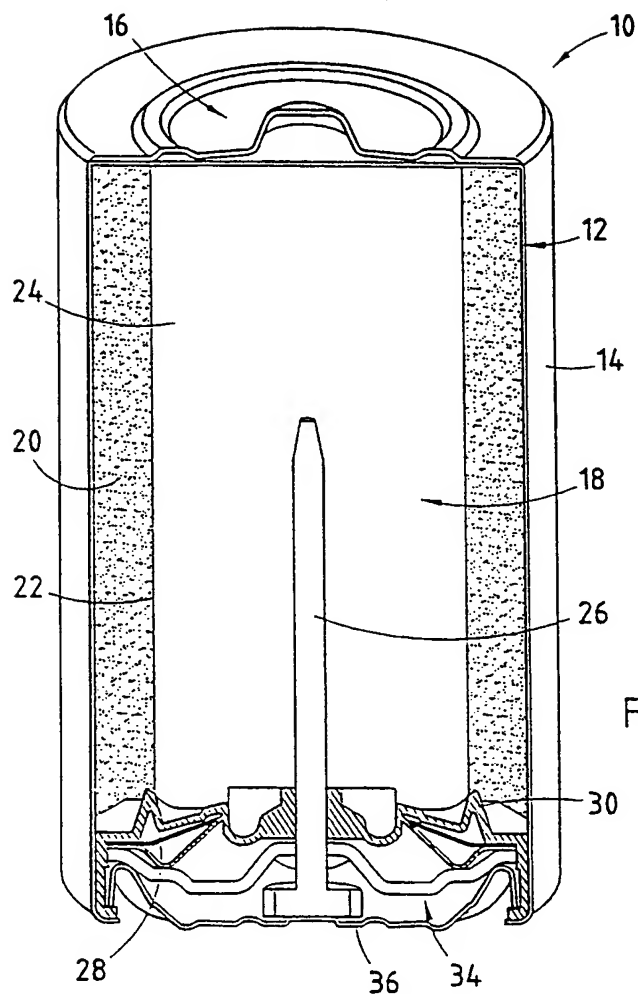


FIG. 1

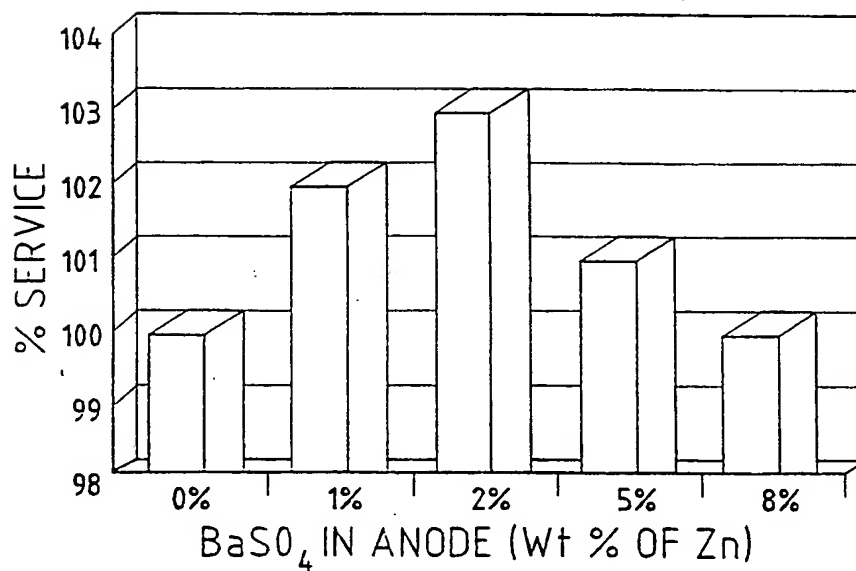
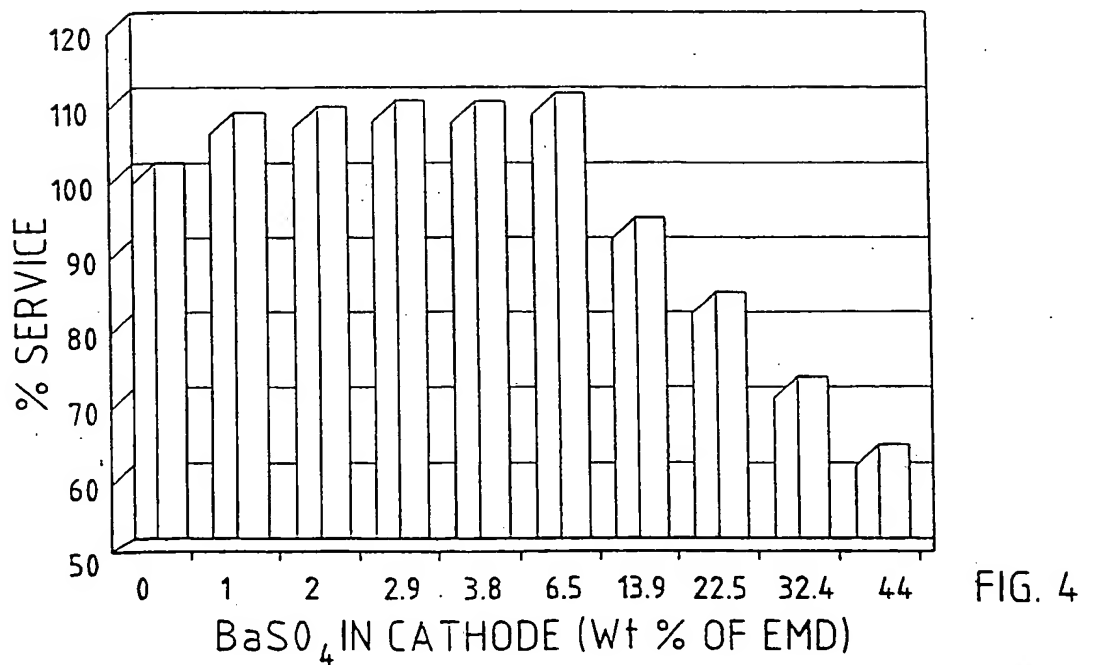
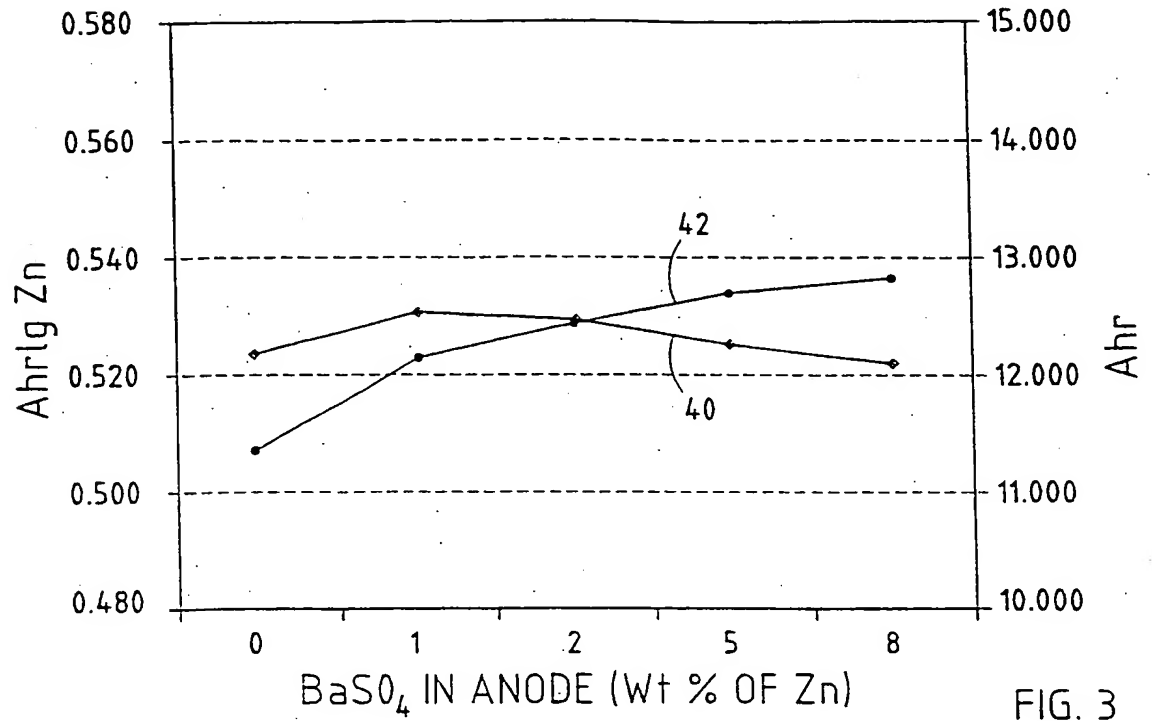


FIG. 2



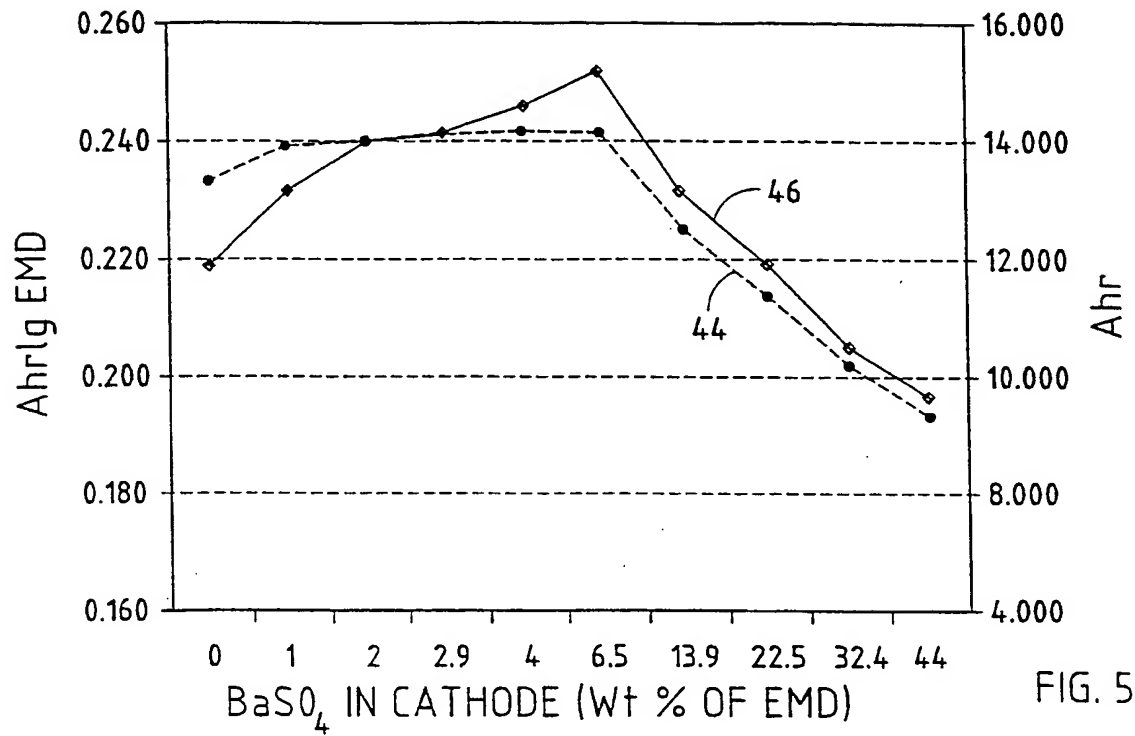


FIG. 5

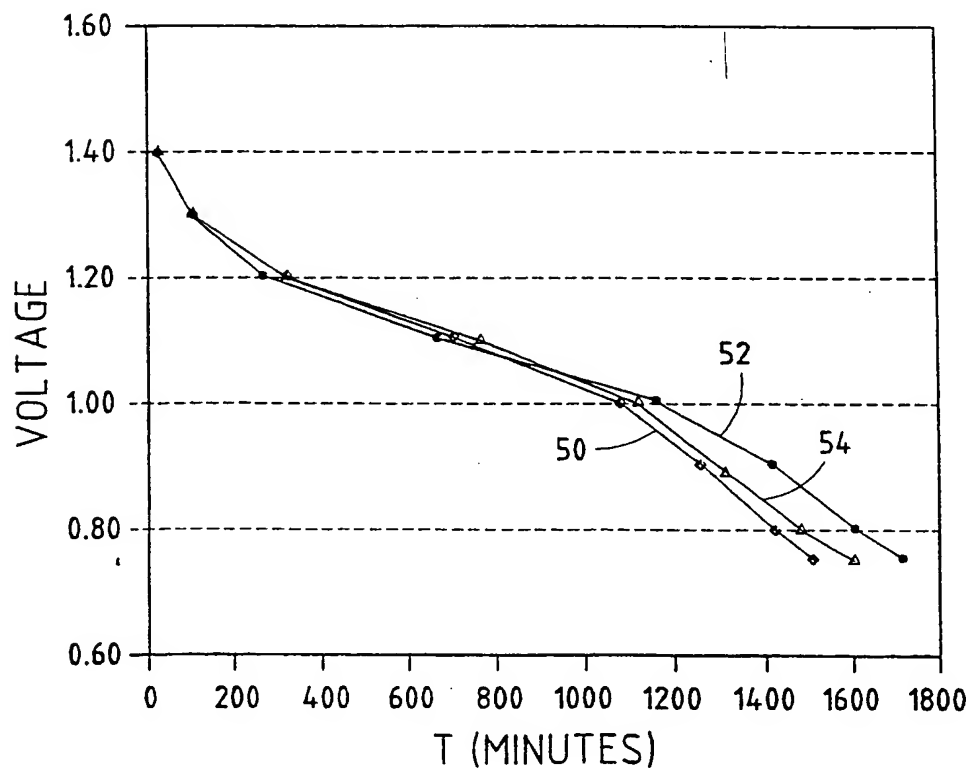


FIG. 6

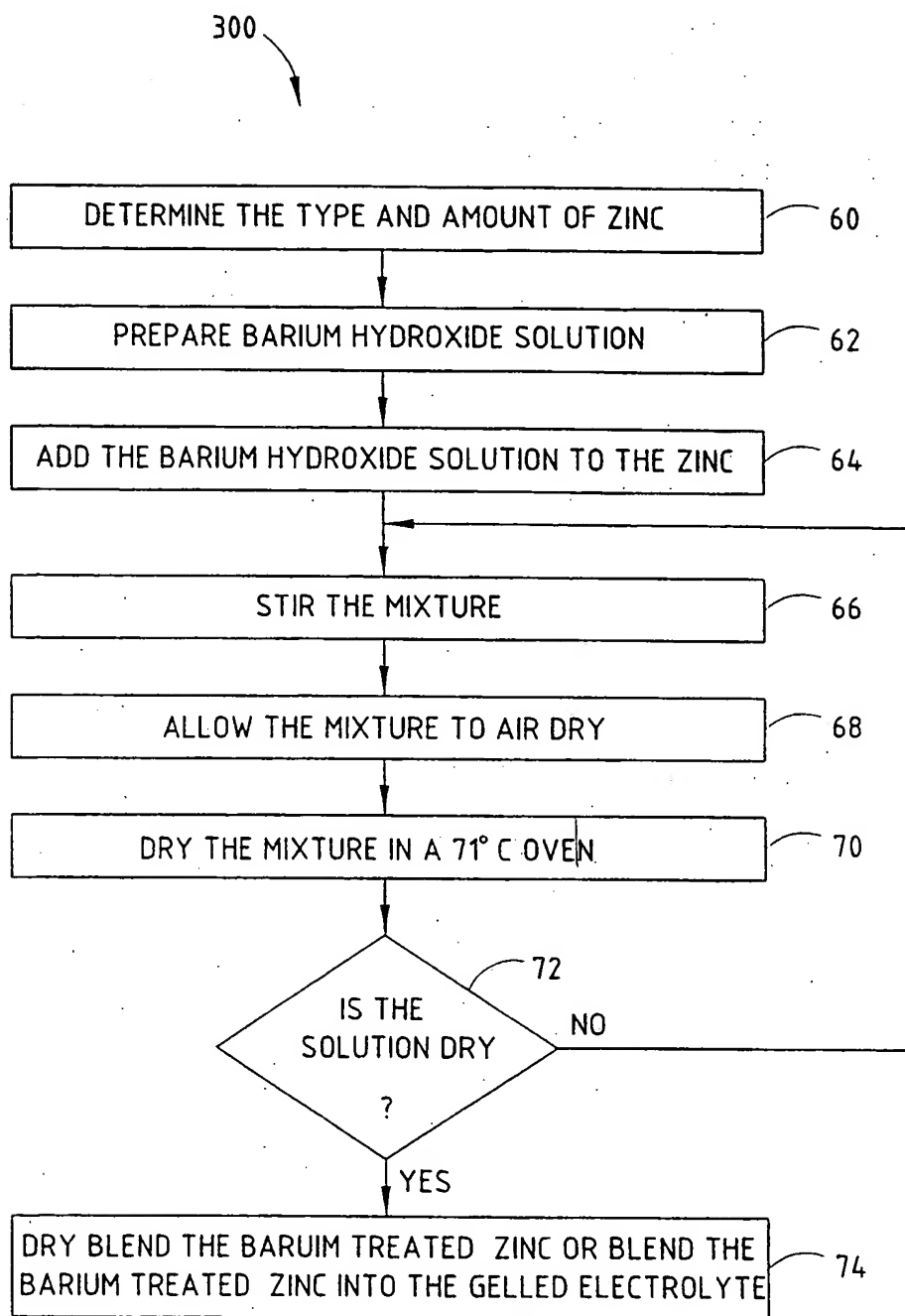
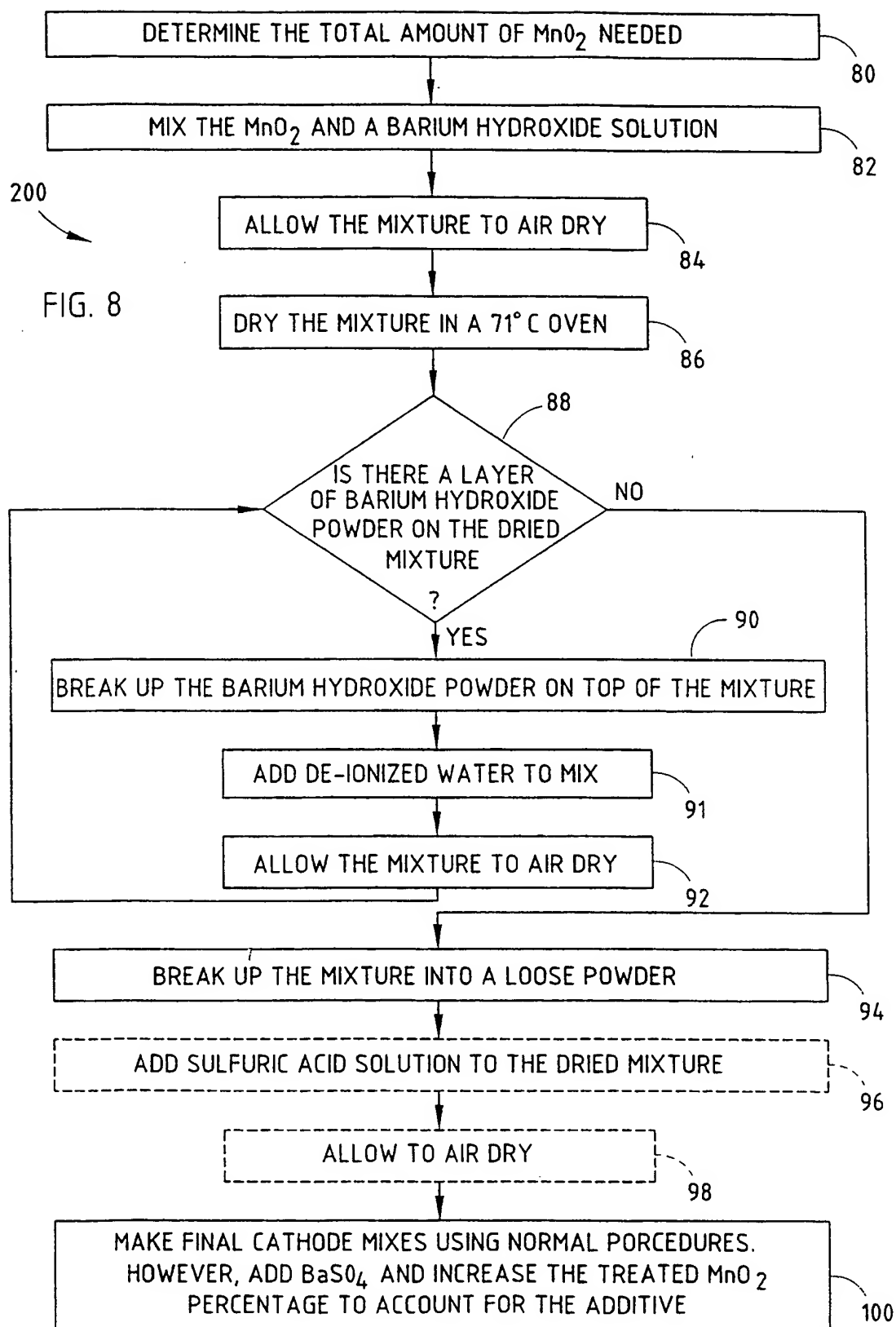


FIG. 7



INTERNATIONAL SEARCH REPORT

Inter: ☐ National Application No

PCT/US 99/26814

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M6/06 H01M4/50 H01M4/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 697 746 A (ENERGY RES CORP) 21 February 1996 (1996-02-21) claim 1	1,3,5
X	WO 93 12551 A (BATTERY TECHNOLOGIES INC) 24 June 1993 (1993-06-24) cited in the application claims 1,2	9-12,17, 20-22
X	US 4 336 315 A (EDA NOBUO ET AL) 22 June 1982 (1982-06-22) column 6, line 1 - line 8; claims 1,6	9-12,17, 20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"B" document member of the same patent family

Date of the actual completion of the international search

15 February 2000

Date of mailing of the international search report

24/02/2000

Name and mailing address of the ISA

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Authorized officer

Andrews, M

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 99/ 26814

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

SEE ADDITIONAL SHEET

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-8, 13-16

An electrochemical cell with Zn anode having a barium compound as additive and method thereof

2. Claims: 9-12, 17-22

An electrochemical cell comprising a cathode active material having barium hydroxide as an additive and method thereof

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Appl. No.

PCT/US 99/26814

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Form PCT/ISA/210 (patent family annex) (July 1992)